



## Covalently bonded 2D/2D O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> heterojunction for enhanced visible-light photocatalytic hydrogen evolution

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### ABSTRACT

Visible-light photocatalytic hydrogen evolution is a key step towards utilizing solar energy. Here we constructed covalently bonded oxidized graphitic C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> (O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>) heterostructure with high surface area via an in-situ solvothermal synthetic strategy. The edge-anchoring of two-dimensional (2D) TiO<sub>2</sub> on 2D O-g-C<sub>3</sub>N<sub>4</sub> was evidenced by the HAADF-STEM EDS mapping, EELS and XPS analysis. Density functional theory computations suggest strong affinity between TiO<sub>2</sub> and O-g-C<sub>3</sub>N<sub>4</sub> 2D structures through N–O–Ti covalent bonding, which drastically enhances the synergistic effect of the light absorption of O-g-C<sub>3</sub>N<sub>4</sub> and high surface area of TiO<sub>2</sub>. The as-formed heterojunction can remarkably boost the visible-light photocatalytic activity for H<sub>2</sub> evolution by 6.1 times compared to physical mixture of TiO<sub>2</sub> nanosheets (NS) and O-g-C<sub>3</sub>N<sub>4</sub>.

### 1. Introduction

Sun, the ultimate energy source of solar system, provides our mother planet with 120 000 TW annually through electromagnetic radiation [1]. Utilization of solar energy by photocatalysis is considered as one of the most promising strategies to meet the increasing energy and environmental demand of human society. In the 1970s, Fujishima and Honda split water into hydrogen and oxygen on sensitized TiO<sub>2</sub> photoanode under irradiation [2]. Since then, the solar-to-fuel conversion through semiconductor photocatalysis has been intensively studied [3–5].

Despite being the earliest milestone in photocatalysis, TiO<sub>2</sub> has never retired from the research frontier [6,7]. The band gap energy of TiO<sub>2</sub> (3.0 eV for rutile phase and 3.2 eV for anatase phase) provides sufficient overpotential to drive most of the desired redox reactions [4]. Stability in aqueous solution and biological nontoxicity made this low cost material commercially applicable on wide scales [8]. However, bulk TiO<sub>2</sub> materials often suffer from poor visible-range absorption (the majority in solar spectra) and rapid recombination of photo-induced electron-hole pairs. Although carrier migration can be facilitated by constructing TiO<sub>2</sub> nanostructures like nanosheets via quantum confinement effect [9], the absorption range remains in the ultraviolet region without elaborate chemical treatment. To tackle this problem, an effective method is to couple TiO<sub>2</sub> with a narrow band-gap material

which provides visible-light absorption and improves separation efficiency of photo-induced charge carriers via formation of heterojunctions [10].

Among the extensively studied narrow band-gap photocatalysts, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has been recently acknowledged as the next-generation photocatalyst by research community [11]. Besides outstanding visible-light response and earth-abundant nature, g-C<sub>3</sub>N<sub>4</sub> is noted for its photostability and chemical tunability, which outperforms a wide range of metal-based narrow-band-gap materials such as Cu<sub>2</sub>O,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and transition metal sulfides [12]. Constructing well-fabricated g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> nanocomposite with enhanced visible-light response is therefore becoming an emerging trend, and lots of synthetic attempts, such as co-calcination [13–21], hydrothermal treatment [22,23], and microwave-assisted synthesis [24], have proven to be successful. Up to now, mesoporous [17], core-shell [18,21], nanotube/nanosheet (1D/2D) [15], nanoparticle/nanosheet (0D/2D) [13,14,19,20,22–24] g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> heterojunctions have been reported. However, most investigations focused on tailoring the composition rather than modifying the interaction type that defines a heterojunction interface. In addition, these reported heterojunctions encounter an inevitable traffic congestion of charge carriers at interfaces [25,26]. The limitation could be surpassed by constructing a well-defined nanosheet/nanosheet (2D/2D) heterojunction [27,28]. Such 2D/2D heterojunction can provide large contact area to facilitate migration of charge carriers at contact

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interfaces and separation of electron-hole pairs, which is beneficial for photocatalytic application [29–31]. Moreover, a high-performance g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> photocatalyst for hydrogen evolution reaction (HER) under visible irradiation has not been reported yet.

In this work, we present a novel self-assembled 2D/2D O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite with enhanced visible-light photocatalytic activity for hydrogen evolution reaction (HER). The applied one-pot solvothermal synthesis is convenient, cost-effective and fluorine-free, while exhibiting high controllability of crystal phase and morphology. Two-dimensional nature of the individual component of the composite grants itself with large specific surface areas, pronounced quantum confinement effect and exposed active sites. The well-defined heterojunction between O-g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> nanosheets is formed via covalent N–O–Ti linkage in-situ which is predicted by density functional theory (DFT) computation and confirmed with EELS and XPS. The strong orbital interactions invoke a band bending at interface, which facilitates migration of photo-induced charge carriers and extend the absorption range.

## 2. Experimental section

### 2.1. Materials

Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer (Pluronic P123, EO<sub>20</sub>PO<sub>70</sub>PEO<sub>20</sub>, M<sub>w</sub> = 5800) was purchased from Sigma-Aldrich (USA). Titanium isopropoxide (TTIP), hydrochloric acid, ethylene glycol, melamine, ethanol, H<sub>2</sub>PtCl<sub>6</sub> and triethanolamine (TEOA) was purchased from Aladdin Industrial Corporation (Shanghai, China). All reagents were used as-received without further purification.

### 2.2. Synthesis of raw TiO<sub>2</sub> nanosheets

The ultrathin TiO<sub>2</sub> nanosheets were prepared using an adopted solvothermal self-assembly method [32,33]. Namely, 1.05 g titanium isopropoxide (TTIP) was added into 0.74 g concentrated HCl under vigorous stirring for 15 min. Meanwhile, 200 mg P123 was dissolved in 3.8 mL ethanol by ultrasonication. The P123 ethanol solution was then added to the above TTIP solution, followed by continuous stirring for another 30 min. 5 mL of the precursor solution with 40 mL ethylene glycol was transferred to an 100 mL Teflon-lined autoclave and heated at 150 °C for 20 h. After cooling down naturally to room temperature, the precipitate was extensively washed with ethanol through centrifugation to remove organic templates and acids. After drying at 60 °C overnight, ca. 100 mg white solid was collected, which was denoted as TiO<sub>2</sub> nanosheets.

### 2.3. Synthesis of raw g-C<sub>3</sub>N<sub>4</sub> nanosheets, O-g-C<sub>3</sub>N<sub>4</sub> and H<sup>+</sup>-g-C<sub>3</sub>N<sub>4</sub>

The raw g-C<sub>3</sub>N<sub>4</sub> was prepared by thermal polymerization of melamine under air atmosphere [14]. In a typical procedure, 20 g of melamine powder was placed in a covered porcelain boat and heated in a muffle furnace at 550 °C for 2 h, at a heating rate of 5 °C/min. The resultant was grinded to yield a yellow powder. To mildly oxidize the g-C<sub>3</sub>N<sub>4</sub> while maintaining the nanosheet morphology, two methods were adopted. The first one is a hydrothermal method [34]. 200 mg g-C<sub>3</sub>N<sub>4</sub> was dispersed in 100 mL deionized water with assistance of 30 min ultrasonication. The suspension was then transferred into a 200 mL Teflon-lined autoclave and heated at 180 °C for 4 h. The resultant was centrifuged and dried overnight at 60 °C, which was denoted as O-g-C<sub>3</sub>N<sub>4</sub>. The second method is an adopted room-temperature acid treatment [35]. 500 mg raw g-C<sub>3</sub>N<sub>4</sub> was added to 12.5 mL of concentrated HCl under vigorously stirring for 1 h. Reaction mixture was filtered, centrifuged and washed for several times to remove excessive HCl. The resultant yellow powder was denoted as H<sup>+</sup>-g-C<sub>3</sub>N<sub>4</sub>.

### 2.4. Synthesis of O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>, H<sup>+</sup>-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composites

All composites were prepared by a bottom-up synthetic strategy of in-situ growth of TiO<sub>2</sub> NS on g-C<sub>3</sub>N<sub>4</sub> substrates. Typically, 100 mg of pretreated or raw g-C<sub>3</sub>N<sub>4</sub> was dispersed in 40 mL ethylene glycol by 30 min ultrasonication in a 100 mL Teflon-liner. 200 mg P123 was dispersed in 3.8 mL absolute ethanol by ultrasonication; 1.1 mL Titanium isopropoxide was added into 0.7 mL concentrated HCl and stirred for 15 min. Then P123 dispersion is added to this mixture, followed by 30 min stirring. 5 mL of mixed solution was transferred to the Teflon-liner with oxidized g-C<sub>3</sub>N<sub>4</sub> suspension and heated at 150 °C for 20 h in an autoclave. The products were washed and centrifuged with deionized water and absolute ethanol for several times to remove organic templates and acids. Yellow precipitations were collected and dried at 60 °C overnight to obtain the final product. For O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>, the ratios of TiO<sub>2</sub> and O-g-C<sub>3</sub>N<sub>4</sub> were varied: 50, 100 and 200 mg O-g-C<sub>3</sub>N<sub>4</sub> were added for samples of O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> 1:2, 1:1 and 2:1, respectively. The catalyst was also prepared by physical mixing the as-synthesized TiO<sub>2</sub> NS and O-g-C<sub>3</sub>N<sub>4</sub> (1:1 weight ratio with respect to TiO<sub>2</sub> NS) and denoted as O-g-C<sub>3</sub>N<sub>4</sub> TiO<sub>2</sub> Mixed.

### 2.5. Characterization

Thermogravimetric (TGA) measurements were performed in a Mettler-Toledo TGA instrument. About 10 mg of each sample was placed in an alumina crucible and heated to 800 °C at a heating rate of 10 °C/min in an air flow. X-ray diffraction (XRD) patterns were acquired on a Rigaku Smartlab-9 kW X-ray diffractometer. Specific surface area and pore structure of each sample were determined by nitrogen sorption analysis using Micromeritics ASAP 2020. The electron microscopy data (EDS, HAADF STEM, EELS) were acquired using the aberration-corrected FEI Titan at 200 kV. The Titan microscope is equipped with an ultra-high brightness gun and super-X EDS detector. The EDS collection efficiency is about 50 times higher than a normal STEM. The EELS spectra were background-subtracted using routine power law method before the N K edge at 400 eV. The energy resolution of the EELS is around 1 eV based on the full width half maximum measurement of the zero loss peak. X-ray photoelectron spectroscopy (XPS) measurement was carried out with Thermo SCIENTIFIC ESCALAB 250Xi instrument using a monochromatized Al K $\alpha$  as the excitation source. C 1 s signal at 284.8 eV was used to calibrate the binding energy (BE) and Shirley-type background was applied for each spectrum. UV-vis diffuse reflectance spectra of the samples were recorded using Lambda 950 UV/Vis/NIR spectrometer (Perkin Elmer) equipped with a diffuse reflectance attachment with a spetralon-cotaed integrating sphere against BaSO<sub>4</sub> reference.

### 2.6. Photocatalytic testing

The photocatalytic HER experiments were performed using an on-line photocatalytic hydrogen generation system (CEL-SPH2N, AuLight, Beijing). A 300 W Xe lamp (CEL-HX300) equipped with a UV cutoff filter (UVIRCUT400, AuLight, Beijing,  $\lambda > 400$  nm) was used as the visible light source, which was fan-cooled during the experiment. To maintain the ambient temperature of reaction system under irradiation, a liquid trap system with water circulation was used. In a typical test, 50 mg of photocatalyst was dispersed in 50 mL of aqueous solution containing 20 vol.% of TEOA, a cheap sacrificial reagent. 3 wt.% of Pt co-catalyst was photo-deposited uniformly on surface of photocatalyst using H<sub>2</sub>PtCl<sub>6</sub> as precursor. Before irradiation, the suspension was degassed thoroughly by evacuation to remove dissolved gases. After an adequate photo-depositing period, the gaseous product was analyzed every hour. H<sub>2</sub> evolution was quantitatively determined by an online gas chromatography (GC-7890, thermal conductivity detector, molecular sieve 5Å, N<sub>2</sub> carrier, Yiyou, Shanghai).

## 2.7. Theoretical computation

DFT computations were performed using the Gaussian 09 program. B3LYP functional is adopted for all computations [36–39]. The LanL2DZ basis set, containing double- $\xi$  valence with effective core potentials (ECPs) of Hay and Wadt, was used for Ti atoms. Polarization functions were also added to Ti ( $f = 1.566$ ) for better precision. For all other atoms including H, C, N and O, 6–311 + G\*\* basis set [40–42] was used. The geometric structures of all species were optimized in the gas phase. Harmonic vibrational frequencies were also computed, whose result showed that all reaction intermediates have no imaginary frequency. Solvation corrections were computed with the same functional and basis sets used in gas phase optimization, based on the gas-phased optimized geometries. SMD (Solvation Model Density) [43] was adopted, with ethylene glycol being the solvent, and temperature is set to be 150 °C. Solvation-corrected Gibbs energy values of all intermediates were calculated. A  $\text{Ti(OH)}_4$  unit was used to represent  $\text{TiO}_2$  oligomer to simplify the calculation. A trimer of basic  $\text{g-C}_3\text{N}_4$  unit was constructed to represent the unoxidized part on O-g-C<sub>3</sub>N<sub>4</sub> nanosheet. To evaluate the thermodynamic feasibility of bonding modes, the change in Gibbs free energy ( $\Delta G$ ) is calculated by  $\Delta G = \Sigma G(\text{products}) - \Sigma G(\text{reactants})$  for the reactions of bond formation. The reactions can be classified into two groups: coordination and condensation. The detailed interpretations for the two types of reactions are provided in Scheme S1.

## 3. Results and discussion

### 3.1. Physico-chemical properties

#### 3.1.1. TGA

TGA measurements (Fig. S1) in flowing air were conducted to ascertain the composition and thermostability of the  $\text{C}_3\text{N}_4/\text{TiO}_2$  composites. The compositions are listed in Table 1. The DTG peak at ca. 300 °C is ascribed to the decomposition of residual P123 on  $\text{TiO}_2$  part, which is hard to remove by ethanol washing [44]. The resulted  $\text{TiO}_2$  weight percentage in the composites is lower than the nominal content.

#### 3.1.2. XRD

The crystalline phases of all precursor nanosheets and composites were determined by X-ray diffraction as shown in Fig. 1. It could be seen in Fig. 1a that  $\text{g-C}_3\text{N}_4$ , O-g-C<sub>3</sub>N<sub>4</sub> and  $\text{H}^+ \text{-g-C}_3\text{N}_4$  all show (100) and (200) characteristic peaks without noticeable shift in diffraction angle, however, the intensities for the oxidized samples are slightly reduced. This result indicates that the crystal structure of  $\text{g-C}_3\text{N}_4$  is predominantly preserved during hydrothermal treatment, while acid treatment leads to structural deterioration, consistent with the

observation from TGA measurements.  $\text{TiO}_2$  nanosheets show peaks with relatively low intensities, which is due to large amount of amorphous  $\text{TiO}_2$  formed in the solvothermal process [44]. The peaks can be assigned to anatase (100), (200) and rutile (110), (220), respectively [33]. The peak intensities of anatase phase are much stronger than those of rutile phase, proving the phase selectivity of this fluorine-free synthetic method. This phase selectivity is maintained in all composite synthesis as shown in Fig. 1b. In addition, the characteristic peaks of  $\text{TiO}_2$  and g-C<sub>3</sub>N<sub>4</sub> were observed without shifts in peak location in these composite samples, which indicates that the in-situ growth did not significantly affect the crystallinity of both nanosheets, irrespective of the amount or type of g-C<sub>3</sub>N<sub>4</sub>.

#### 3.1.3. $\text{N}_2$ sorption

$\text{N}_2$  sorption measurements were performed to investigate the textural characteristics of the obtained materials. Fig. S2 shows the  $\text{N}_2$  sorption isotherms and the corresponding pore size distribution and Table 1 summarizes  $S_{\text{BET}}$ ,  $V_{\text{tot}}$ ,  $V_{\text{meso}}$  and average pore size. All isotherms are of type IV with H4 type hysteresis loops, indicating the co-existing of micropores and slit-shaped mesopores caused by the stacking of thin nanosheets, which can be observed from the wrinkles and irregular folding structures in the TEM images (Figs. S3 and S4). The  $S_{\text{BET}}$  of  $\text{TiO}_2$  NS is  $330 \text{ m}^2 \text{ g}^{-1}$ , close to the reported result [33]. The g-C<sub>3</sub>N<sub>4</sub> family presents much smaller  $S_{\text{BET}}$  and lower porosity than  $\text{TiO}_2$  NS, even though mild oxidation by hydrothermal treatment increases  $S_{\text{BET}}$  to  $55 \text{ m}^2 \text{ g}^{-1}$  and  $V_{\text{tot}}$  to  $0.20 \text{ cm}^3 \text{ g}^{-1}$ . To be noted, the average pore size for the g-C<sub>3</sub>N<sub>4</sub> family is much larger than  $\text{TiO}_2$  NS, indicating the larger nanosheets size of the former. The composite samples all show higher  $S_{\text{BET}}$  and  $V_{\text{tot}}$  than their correspondent precursor g-C<sub>3</sub>N<sub>4</sub>. The increase in the porosity is ascribed to the  $\text{TiO}_2$  component in the composite. O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> 1:1 possesses  $S_{\text{BET}}$  of  $263 \text{ m}^2 \text{ g}^{-1}$ ,  $V_{\text{tot}}$  of  $0.57 \text{ cm}^3 \text{ g}^{-1}$ , and average pore size of 14.7 nm.  $\text{TiO}_2$  in O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> 1:1 is likely to embody similar textural properties to that in  $\text{TiO}_2$  NS. The even larger  $V_{\text{tot}}$  and average pore size of the composite than those of  $\text{TiO}_2$  NS are ascribed to the presence of O-g-C<sub>3</sub>N<sub>4</sub>. Further increasing the amount of O-g-C<sub>3</sub>N<sub>4</sub>, however, reduces the porosity, since the porosity and surface area are mainly contributed by  $\text{TiO}_2$  part. It is speculated that the introduction of O-g-C<sub>3</sub>N<sub>4</sub> in the solvothermal synthesis does not exert significant influence on the templated growth and aggregation state of  $\text{TiO}_2$  nanosheets. g-C<sub>3</sub>N<sub>4</sub> may also not interfere much, due to few functional groups at its surface. Nevertheless,  $\text{H}^+ \text{-g-C}_3\text{N}_4$  probably results in some aggregation of  $\text{TiO}_2$  NS due to protonation of amine groups caused by acid treatment, leading to the relatively less porosity.

**Table 1**  
Physico-chemical properties of  $\text{C}_3\text{N}_4/\text{TiO}_2$  composites and the precursors.

Entry	Catalyst	$\text{TiO}_2$ <sup>a</sup> (wt.%)	$S_{\text{BET}}$ <sup>b</sup> ( $\text{m}^2 \text{ g}^{-1}$ )	$V_{\text{tot}}$ <sup>c</sup> ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{\text{meso}}$ <sup>d</sup> ( $\text{cm}^3 \text{ g}^{-1}$ )	Average pore size <sup>e</sup> (nm)
1	O-g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> 1:1	37	263	0.57	0.53	8.7
2	O-g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> 1:2	50	287	0.60	0.54	8.4
3	O-g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> 2:1	21	171	0.43	0.40	10.1
4	g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> 1:1	39	259	0.48	0.42	7.3
5	$\text{H}^+ \text{-g-C}_3\text{N}_4/\text{TiO}_2$ 1:1	33	163	0.17	0.13	4.3
6	O-g-C <sub>3</sub> N <sub>4</sub> TiO <sub>2</sub> Mixed	35	n.d.	n.d.	n.d.	n.d.
7	$\text{TiO}_2$ NS	59	330	0.41	0.36	5.0
8	g-C <sub>3</sub> N <sub>4</sub>	0	12	0.12	0.12	43.5
9	O-g-C <sub>3</sub> N <sub>4</sub>	0	55	0.20	0.20	14.7
10	$\text{H}^+ \text{-g-C}_3\text{N}_4$	0	19	0.12	0.12	25.8

<sup>a</sup> The  $\text{TiO}_2$  content in the composite or  $\text{TiO}_2$  NS is determined from TGA.

<sup>b</sup> Surface area ( $S_{\text{BET}}$ ) is calculated by the Brunauer-Emmett-Teller (BET) method.

<sup>c</sup> Total pore volume ( $V_{\text{tot}}$ ) was calculated from the saturation plateau at high relative pressures.

<sup>d</sup> Mesopore volume ( $V_{\text{meso}}$ ) was calculated after subtraction of the micropore volume as obtained by the t-plot method.

<sup>e</sup> Average pore size was calculated from adsorption branches of the isotherms, based on the Barrett-Joyner-Halenda (BJH) model.

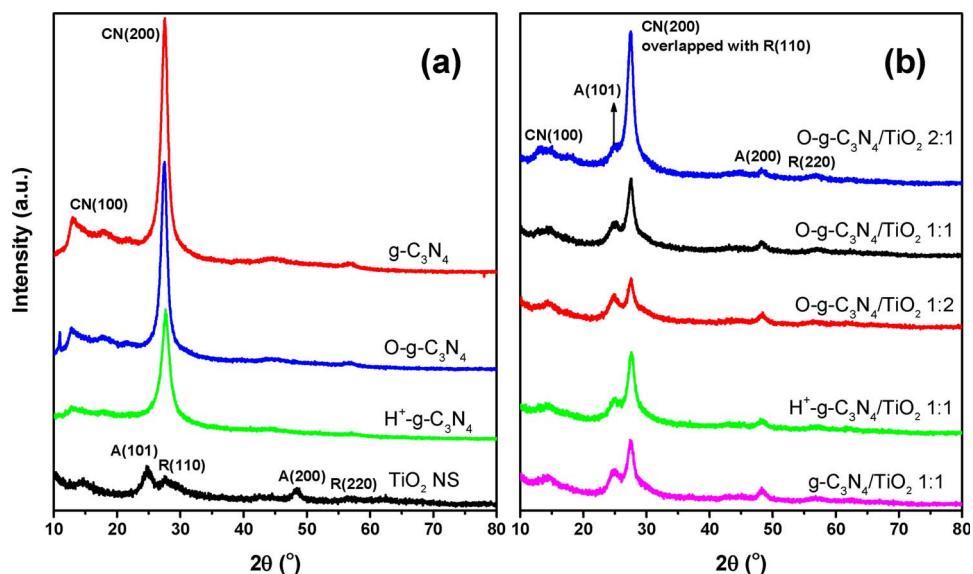


Fig. 1. XRD patterns of (a)  $\text{TiO}_2$  NS,  $\text{g-C}_3\text{N}_4$ ,  $\text{O-g-C}_3\text{N}_4$ ,  $\text{H}^+ \text{-g-C}_3\text{N}_4$  and (b) composites of  $\text{O-g-C}_3\text{N}_4/\text{TiO}_2$  with ratios of 1:1, 1:2, 2:1,  $\text{g-C}_3\text{N}_4/\text{TiO}_2$  1:1 and  $\text{H}^+ \text{-g-C}_3\text{N}_4/\text{TiO}_2$  1:1.

### 3.2. Investigation on interfacial covalent bonding

#### 3.2.1. Elemental distribution at interface

High-angle annular dark-field scanning TEM (HAADF-STEM) imaging of  $\text{O-g-C}_3\text{N}_4/\text{TiO}_2$  1:1 shows fine interfacial structures. It can be seen in Fig. 2a that small ultrathin leaf-shaped nanosheets (around 50 nm) grow on the edge of much larger nanosheets. The elemental composition was revealed by energy-dispersive X-ray spectroscopy (EDS) mappings as shown in Fig. 2b–e. Overall morphology and elemental mapping can be found in Fig. S5. Elemental distribution indicates that the large nanosheet is  $\text{O-g-C}_3\text{N}_4$  and the small nanoleaves at its edges are  $\text{TiO}_2$ . The individually grown ultrathin  $\text{TiO}_2$  nanosheets, formed by template-assisted self-assembly, show extensive surface area which is evidenced by  $\text{N}_2$  sorption results.

To investigate the interface between the two components, electron energy loss spectra (EELS) were obtained at different interface regions 1 and 2, and also at the pure  $\text{TiO}_2$  leaf region, as is shown in Fig. 2f. N K

edge, Ti L edge and O K edge can be observed at both interface regions 1 and 2. At the pure  $\text{TiO}_2$  leaf region, only two-peak feature of the Ti L3 and L2 edge can be seen. No octahedral crystal field splitting feature is observed in the as-formed  $\text{TiO}_2$ , indicating a likely poor crystallinity of  $\text{TiO}_2$  leaves. It corresponds well to the low-intensity XRD peaks as discussed earlier. The Ti and O signals increase and N K edge decreases in intensity gradually as it goes further away from the (“root”) interface area. Both the Ti and N EELS edges are very pronounced at the interface, indicating the formation of the connected  $\text{O-g-C}_3\text{N}_4/\text{TiO}_2$  heterojunction. In contrast, the N K edge disappears in the pure  $\text{TiO}_2$  leaf region. The EELS results are in good agreement with the EDS mapping as shown in Fig. 2g. In addition, the O K edge for the  $\text{TiO}_2$  leaf shows a clear two-peak feature in Fig. 2g. Peak 1 is narrower and sharper than peak 2 at the  $\text{TiO}_2$  leaf. The O K edge peak 1 and 2 are wider at the interface region than the pure  $\text{TiO}_2$  region. Based on the plural scattering theory, the peaks 1 and 2 are impacted heavily by the scattering of the fast electrons by the first and second nearest coordination shells

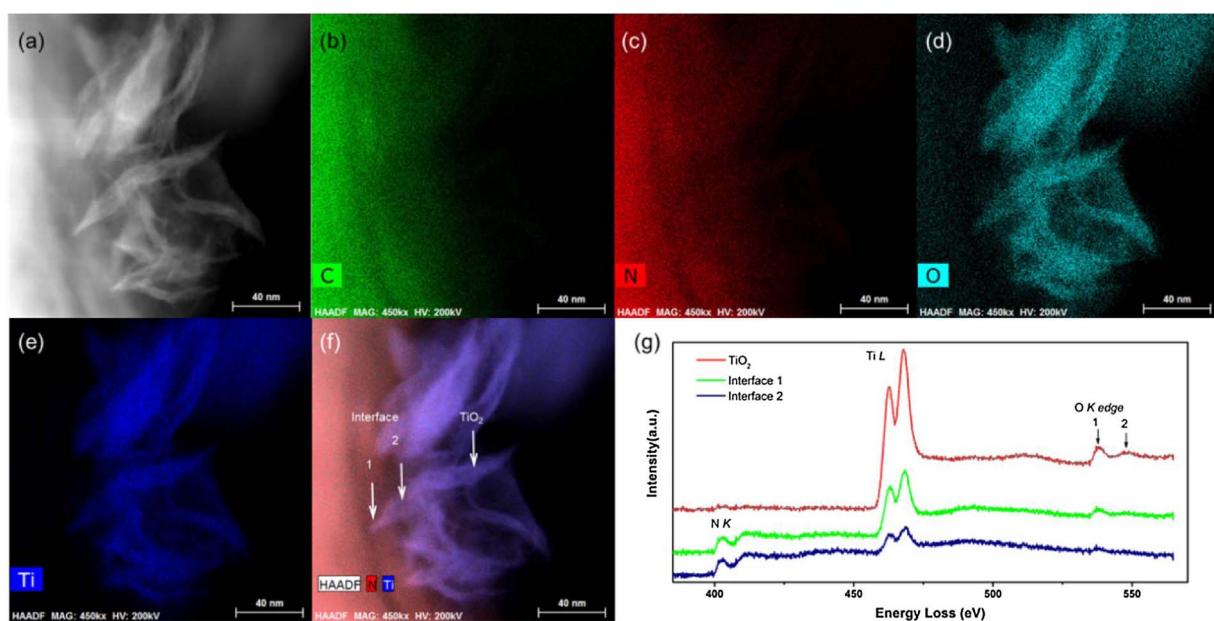


Fig. 2. (a) Representative HAADF-STEM image of  $\text{O-g-C}_3\text{N}_4/\text{TiO}_2$  1:1 and (b) C, (c) N, (d) O, and (e) Ti EDS elemental maps of the corresponding area. (f) Superposed N, Ti and HAADF maps showing the interface regions and  $\text{TiO}_2$  leaves. (g) EELS spectra from interface and  $\text{TiO}_2$  region showing the N K edge, Ti L edge, and O K edge.

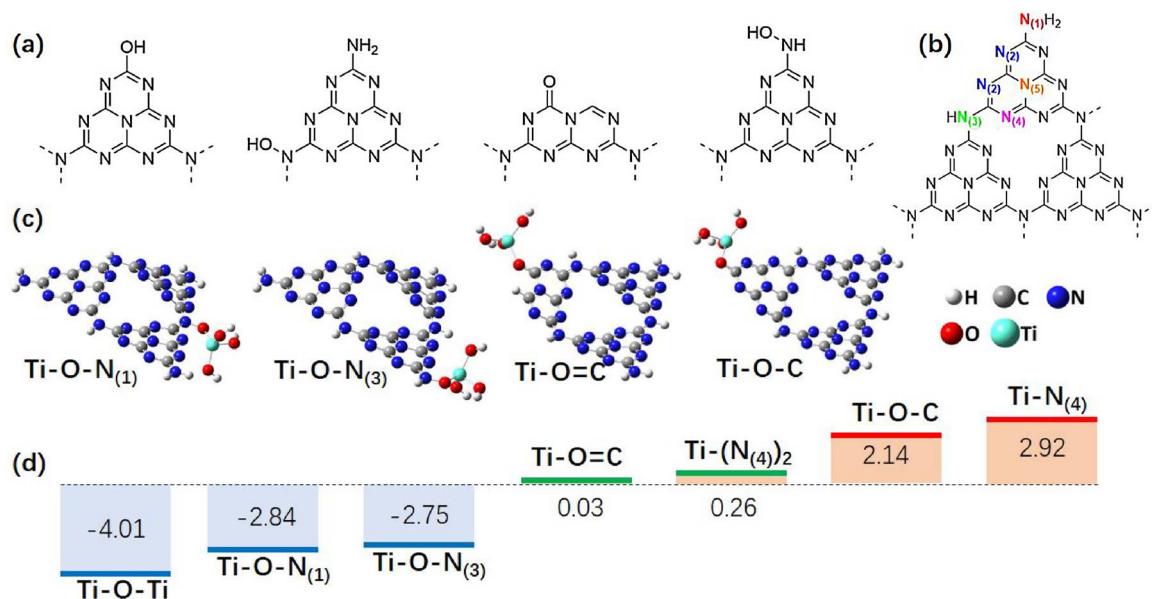


Fig. 3. (a) The functional groups introduced by mild oxidation, (b) different nitrogen sites on  $\text{g-C}_3\text{N}_4$ , (c) Bonding modes between  $\text{O-g-C}_3\text{N}_4$  and  $\text{TiO}_2$ , and (d)  $\Delta G$  of selected bonding modes (kcal/mol).

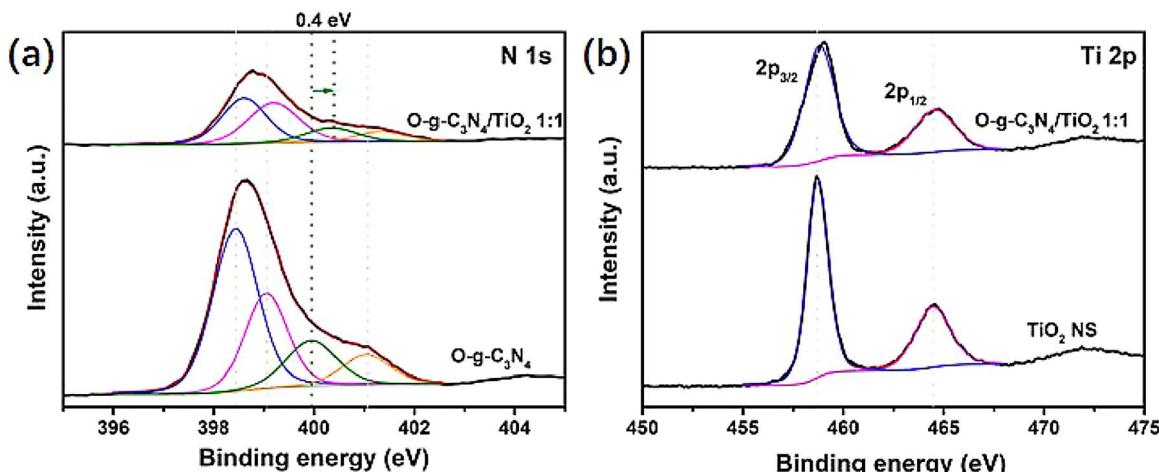


Fig. 4. XPS spectra of N 1s and Ti 2p in  $\text{O-g-C}_3\text{N}_4/\text{TiO}_2$ ,  $\text{O-g-C}_3\text{N}_4$  and  $\text{TiO}_2$  NS.

around the O atoms, respectively [45]. The fact that the peaks of the O K edge get wider indicates the increased degree of disorder of the oxygen coordination environment at interfaces [45,46], probably resulting from the covalent bonding between  $\text{TiO}_2$  NS and  $\text{O-g-C}_3\text{N}_4$  formed during the solvothermal process.

### 3.2.2. DFT calculation

To investigate the bonding modes between  $\text{O-g-C}_3\text{N}_4$  and  $\text{TiO}_2$  nanosheets under solvothermal condition, thermodynamic calculations were conducted. A series of functional groups (Fig. 3a), which can be introduced to the edges of  $\text{g-C}_3\text{N}_4$  by mild oxidation [34,35], were added to basic  $\text{g-C}_3\text{N}_4$  unit to simulate oxidized  $\text{O-g-C}_3\text{N}_4$  edges. Different nitrogen sites on  $\text{O-g-C}_3\text{N}_4$  were treated respectively, as shown in Fig. 3b. P123 was neglected in this study to avoid otherwise huge computational cost. It is worth noting that the structural optimization leads to an energetically stable corrugated conformation of  $\text{g-C}_3\text{N}_4$  rather than a planar one under solvothermal condition, as is shown in Fig. S6. The ridges form from corrugation, exposing active sites while keeping the band structure unchanged [47].

The Gibbs free energy change ( $\Delta G$ ) of formation of different bonding modes between  $\text{Ti}(\text{OH})_4$  unit and  $\text{O-g-C}_3\text{N}_4$  and selected N-Ti,

O-Ti distances are summarized in Table S1, and the corresponding optimized structures are shown in Fig. S7. All coordination bonding modes were calculated to be thermodynamically infeasible ( $\Delta G > 0$ ), including coordination of Ti with any C, O and N sites on  $\text{O-g-C}_3\text{N}_4$  (Table S1, 1–13). Calculations also suggest that Ti–OH cannot condense with C–OH or N–H on  $\text{O-g-C}_3\text{N}_4$  (Table S1, 14–16). The only two thermodynamically feasible linkages between  $\text{TiO}_2$  and  $\text{O-g-C}_3\text{N}_4$  are the  $\text{N}_{(1)}\text{–O–Ti}$  and  $\text{N}_{(3)}\text{–O–Ti}$  that form through condensation between N–OH and Ti–OH. The formation is partially due to the stabilizing effect of neighboring N atoms. Therefore the calculations suggest a stronger affinity between  $\text{TiO}_2$  oligomer and oxidized edges of  $\text{O-g-C}_3\text{N}_4$  compared to its unoxidized regions. The four bonding modes enabled by the presence of oxygen-containing functional groups ( $\text{N}_{(1)}\text{–OH}$ ,  $\text{N}_{(3)}\text{–OH}$ ,  $\text{C}=\text{O}$ ,  $\text{C–OH}$ ) on  $\text{O-g-C}_3\text{N}_4$  edges and seven bonding modes with the lowest  $\Delta G$  are shown in Fig. 3c and d. The calculation results provide evidence for covalent bonding at composite interface through N–O–Ti bonding.

### 3.2.3. XPS

The bonding modes of  $\text{O-g-C}_3\text{N}_4$ ,  $\text{TiO}_2$  and  $\text{O-g-C}_3\text{N}_4/\text{TiO}_2$  are analyzed by XPS as shown in Fig. 4. In the deconvoluted N 1s spectrum

of O-g-C<sub>3</sub>N<sub>4</sub>, four peaks at about 398.4, 399.0, 399.9 and 401.0 eV can be assigned to nitrogen in C–N, C=N, N–O and N–H bonds, respectively [34]. These four peaks can also be observed in the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite, however, the peak corresponding to N–O shifted to higher binding energy (BE) by 0.4 eV, which should be caused by formation of N–O–Ti as predicted by DFT calculation. Electron-deficient Ti atom tends to lower the electron density of N–O system via Ti–O bond, weakening the shielding effect of N valence electrons, which increases the BE of N 1s electrons. The Ti 2p spectra of pure TiO<sub>2</sub> and composite both showed peaks of Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> at 458.7 and 464.4 eV, respectively [48]. There was no significant shift in BE of both peaks, which suggests the chemical state of Ti is not altered during solvothermal process regardless of the presence of O-g-C<sub>3</sub>N<sub>4</sub>. The well-fitted two peaks clearly exclude the presence of Ti–C [22], Ti–N [22] and Ti<sup>3+</sup> [23] which, if exist, should have Ti 2p<sub>3/2</sub> peaks located at 460.8, 462.1 and 463.3 eV, respectively. The XPS spectra of C 1s and O 1s (Fig. S8) cannot provide concrete evidence for N–O–Ti formation due to interference of adsorbed P123 surfactant.

### 3.2.4. Formation mechanism

Based on above experimental and theoretical results, a mechanism for the composite formation can be proposed as shown in Scheme 1. First, TTIP forms hydrated TiO<sub>2</sub> precursor oligomers during controlled hydrolysis. The oligomers are then confined inside the inverse lamellar micelles of P123 through hydrogen bonds in EG solution [33]. The tiny layered oligomer agglomerates are attached to edges of O-g-C<sub>3</sub>N<sub>4</sub> via N–O–Ti covalent linkage. Thereafter, the attached oligomer agglomerates grows in-situ into leaf-shaped ultrathin TiO<sub>2</sub> nanosheets. After template removal, the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> covalent heterojunction is successfully fabricated. The formation of N–O–Ti linkage at the interfaces could facilitate the separation and migration of photo-induced charge carriers through the heterojunction, which can improve the optical and photoelectrochemical properties.

### 3.3. Optical properties and photocatalytic activities

#### 3.3.1. UV-vis DRS

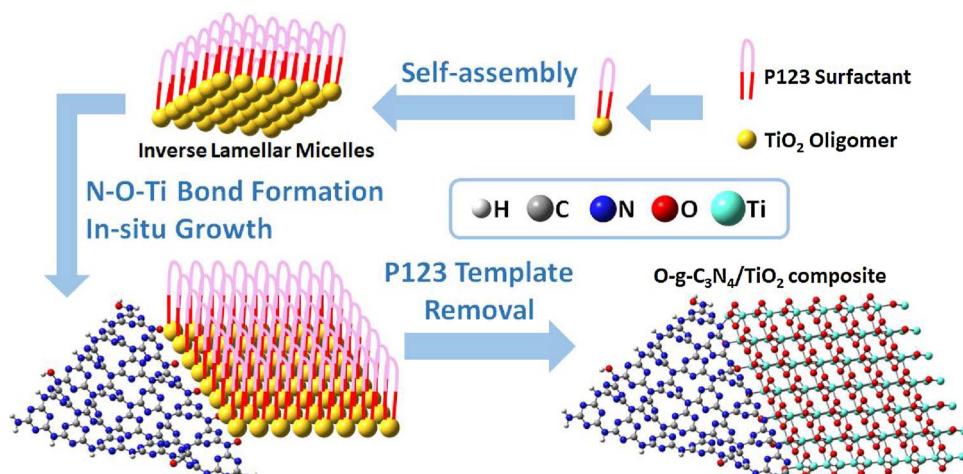
UV-vis diffuse reflection spectra were collected and analyzed to investigate optical absorption and band structure of all samples (Fig. 5). As shown in Fig. 5a, TiO<sub>2</sub> nanosheets have outstanding UV absorption but zero absorption above 400 nm. In contrast, the raw g-C<sub>3</sub>N<sub>4</sub> has a superior visible-range absorption. Both oxidation methods, namely hydrothermal and acid treatments, only introduced minor defects and functional groups which do not alter absorption range dramatically. Fig. 5b displays the UV-vis absorption spectra of all composites. The g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> 1:1 composite exhibits no apparent widening in absorption

range, which can be explained by absence of effective linkages between TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> nanosheets as suggested by DFT calculation. On the contrary, O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> and H<sup>+</sup>-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composites show broader absorption range due to formation of covalent heterojunctions via N–O–Ti bonds. Among all composites the O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> 1:1 sample experiences the most pronounced broadening in absorption range.

The corresponding band gap energy can be derived according the Kubella-Munk function [49], as is shown in Fig. 5c and d. The g-C<sub>3</sub>N<sub>4</sub> family was treated as direct gap semiconductor while all other samples were treated as indirect ones. The g-C<sub>3</sub>N<sub>4</sub> family has narrower band gap than TiO<sub>2</sub> nanosheets. Mild oxidation resulted in a slight change in band gap energy of g-C<sub>3</sub>N<sub>4</sub>. However, all of the composites showed significantly narrower band gap than any of the pure nanosheets. The decrease in band gap energy is likely caused by the formation of heterojunction between two materials with staggered band structures. O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> has the narrowest band gap among the three composite types, suggesting a stronger interaction at its heterojunction interfaces than those of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> and H<sup>+</sup>-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>. By reducing the ratio of TiO<sub>2</sub> and O-g-C<sub>3</sub>N<sub>4</sub> in the composite, the contribution of such effect can be strengthened, leading to a narrower band gap and therefore extending the spectral response. Band gap tuning in similar composite systems can be achieved by functionalizing the precursors as well as adjusting the composition.

#### 3.3.2. Photocatalytic hydrogen evolution

The photocatalytic activity of the as-prepared samples was evaluated by hydrogen evolution from water under visible-light irradiation (wavelength > 400 nm). TiO<sub>2</sub> exhibits no photocatalytic activity since its bandgap energy is too high for visible-light to induce electron excitation. g-C<sub>3</sub>N<sub>4</sub> showed a low hydrogen evolution of 180.5  $\mu\text{mol g}^{-1} \text{h}^{-1}$ , suffering from fast recombination of photo-induced electron-pairs and small surface area. The problem is not settled even after mild oxidation, with O-g-C<sub>3</sub>N<sub>4</sub> and H<sup>+</sup>-g-C<sub>3</sub>N<sub>4</sub> exhibiting just slightly improved photocatalytic activity. In contrast, all composite samples display a significant boost in hydrogen evolution. The O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> 1:1 composite shows the best performance in hydrogen evolution, reaching 587.1  $\mu\text{mol g}^{-1} \text{h}^{-1}$  which is 6.1 times the physical mixture, and 3.2 times the pure O-g-C<sub>3</sub>N<sub>4</sub>. This boost in photocatalytic activity can be attributed to the formation of covalent bonding at heterojunction interfaces. Through N–O–Ti linkage which is predicted by DFT computation and confirmed by XPS and EELS, the photo-induced electrons from O-g-C<sub>3</sub>N<sub>4</sub> can migrate to TiO<sub>2</sub> with high efficiency and the recombination of photo-induced electron-hole pairs is suppressed. The efficient heterojunction may also lead to band bending at the interface region, which lowers the local band gap energy and broadens



Scheme 1. Schematic of the synthesis of O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite.

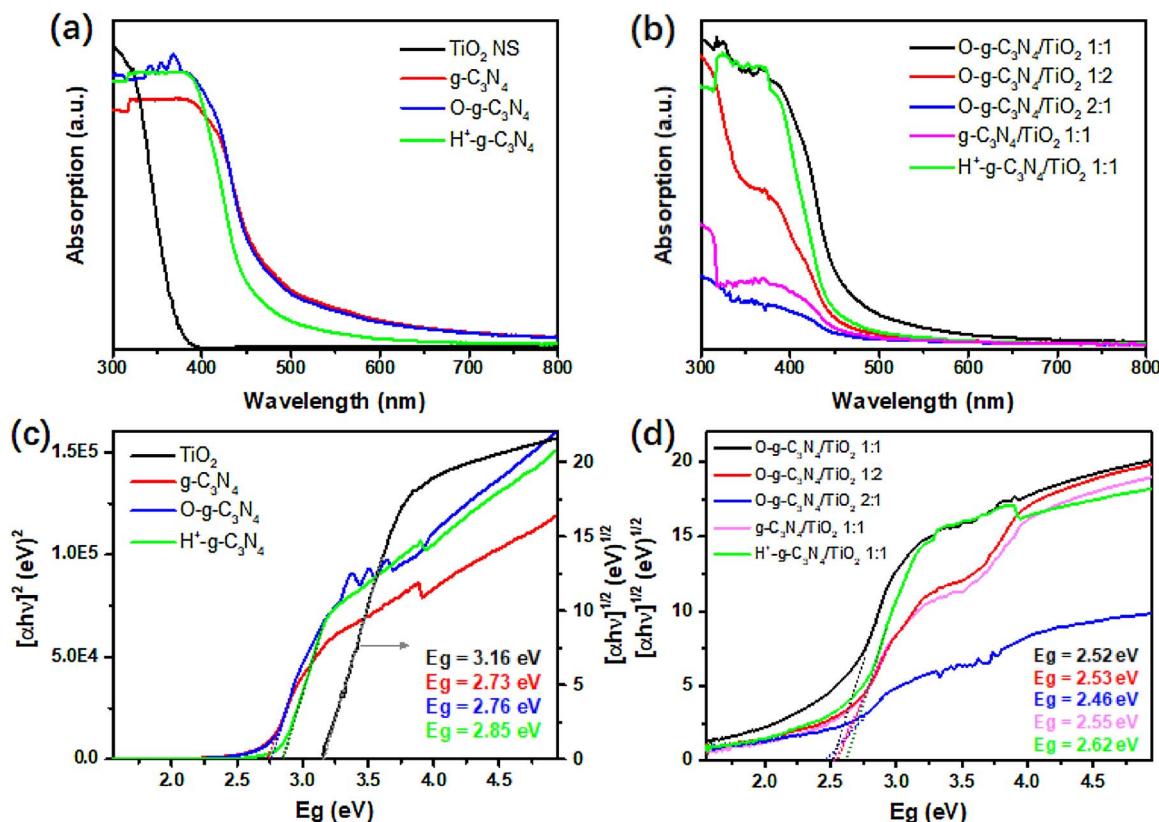


Fig. 5. UV-vis DRS of (a)  $\text{TiO}_2$  NS,  $\text{g-C}_3\text{N}_4$ ,  $\text{O-g-C}_3\text{N}_4$ ,  $\text{H}^+ \text{-g-C}_3\text{N}_4$  and (b) composites of  $\text{O-g-C}_3\text{N}_4/\text{TiO}_2$  with ratios of 1:1, 1:2, 2:1,  $\text{g-C}_3\text{N}_4/\text{TiO}_2$  1:1 and  $\text{H}^+ \text{-g-C}_3\text{N}_4/\text{TiO}_2$  1:1. (c, d) Corresponding plots of  $(\alpha h\nu)^2$  or  $(\alpha h\nu)^{1/2}$  versus photon energy ( $h\nu$ ) for the band gap energies of samples in (a, b).

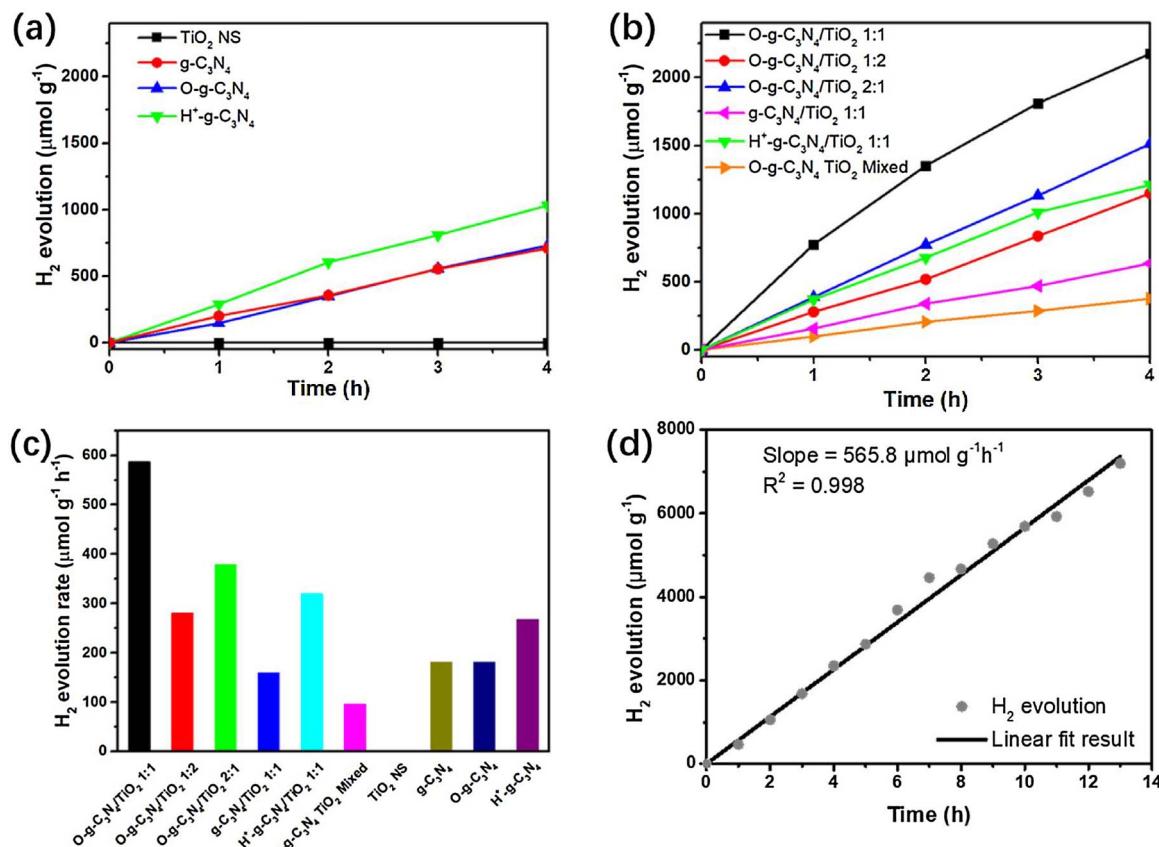
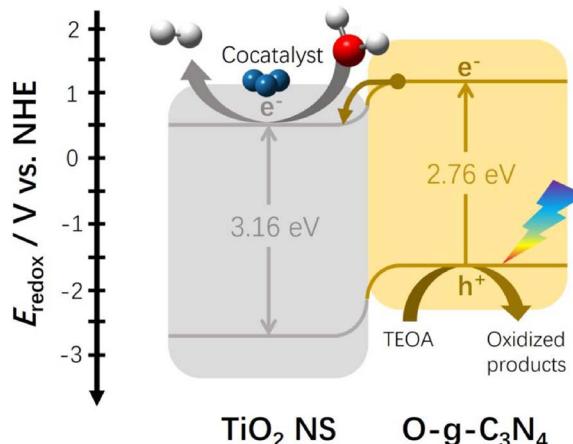


Fig. 6. Hydrogen evolution plot versus time of (a)  $\text{TiO}_2$  NS,  $\text{g-C}_3\text{N}_4$ ,  $\text{O-g-C}_3\text{N}_4$ ,  $\text{H}^+ \text{-g-C}_3\text{N}_4$  and (b) composites of  $\text{O-g-C}_3\text{N}_4/\text{TiO}_2$  with ratios of 1:1, 1:2, 2:1,  $\text{g-C}_3\text{N}_4/\text{TiO}_2$  1:1,  $\text{H}^+ \text{-g-C}_3\text{N}_4/\text{TiO}_2$  1:1 and  $\text{O-g-C}_3\text{N}_4 \text{ TiO}_2$  Mixed. (c) Hydrogen evolution rates of all tested photocatalysts. (d) Stability test of  $\text{O-g-C}_3\text{N}_4/\text{TiO}_2$  1:1 sample under the same reaction conditions.



**Scheme 2.** Proposed mechanism for photocatalytic hydrogen evolution on O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> 1:1 composite under visible-light irradiation.

the absorption range [50,51]. In addition, the 2D nanostructure provides large specific surface area for cocatalyst loading, reactant adsorption and mass transfer acceleration. To optimize the benefits from all discussed effects, composites made with various weight ratios of O-g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> were tested. The 1:1 ratio was found to maximize the construction of N–O–Ti heterojunction without compromising the merit of specific surface area. Fig. 6d shows the stability test result for O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> 1:1 sample under the same reaction conditions. The hydrogen evolution rate stays at about 565.8 μmol g<sup>-1</sup> h<sup>-1</sup> during the 13-h irradiation, indicating that the as-fabricated N–O–Ti covalent heterojunction successfully achieves remarkably high photocatalytic activity as well as stability. With facile preparation and remarkably enhanced photocatalytic activity, the as-prepared O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> might provide insights for design and synthesis of high-performance O-g-C<sub>3</sub>N<sub>4</sub>/metal oxide photocatalysts with covalent heterojunctions.

The mechanism for photocatalytic HER on O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite under visible-light irradiation is illustrated in **Scheme 2**. Incident photons with sufficient energy excite electrons in valence band of O-g-C<sub>3</sub>N<sub>4</sub> to its conduction band. The photo-induced holes in valence band of O-g-C<sub>3</sub>N<sub>4</sub> are captured by TEOA, while the photo-induced electrons migrate through covalent N–O–Ti heterojunction into the valence band of TiO<sub>2</sub> nanosheets. The photo-induced electrons finally reach uniformly deposited Pt cocatalyst at vast TiO<sub>2</sub> surface where the electrons reduce water to hydrogen gas. Heterojunction defined by N–O–Ti linkages results in efficient charge carrier separation at interfaces and band bending effect which further widens the absorption range, enhancing the photocatalytic activity of the composite.

#### 4. Conclusions

Covalently bonded O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> heterojunctions were successfully fabricated via a facile one-pot solvothermal synthetic method. In this strategy, using O-g-C<sub>3</sub>N<sub>4</sub> as the substrate and P123 as the soft templating agent, ultrathin and uniform TiO<sub>2</sub> nanoleaves grew in-situ onto O-g-C<sub>3</sub>N<sub>4</sub> edges. The N–O–Ti covalent bonding at heterojunction interfaces is evidenced by experimental characterization and DFT computation. Compared to composites derived from other types of g-C<sub>3</sub>N<sub>4</sub> precursors (raw g-C<sub>3</sub>N<sub>4</sub> and H<sup>+</sup>-g-C<sub>3</sub>N<sub>4</sub>) and physical mixture, O-g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> exhibited superior visible-light activity and high stability for photocatalytic hydrogen evolution reaction, due to the facilitated charge carrier migration through the heterojunction defined by covalent interfacial N–O–Ti bonding.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apcatb.2017.12.066>.

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